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Measurement and correlation of solubility of carbendazim in lower alcohols

Xiao Zhang, Liangcheng Song*, Danyang Zhao, Di Wu, Chongqiang Zhu, Chunhui Yang

School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, People's Republic of China

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ABSTRACT

The solubility of carbendazim in the lower alcohols (Methanol, Ethanol, *n*-Propanol, *n*-Butanol, and *n*-Pentanol) at temperatures from 278.15 K to 323.15 K was measured by a dynamic thermodynamic equilibrium method. The solubility of carbendazim increased with the increasing temperature in each solvent. The experimental data were well correlated by Apelblat equation, and the dissolving enthalpy and entropy were calculated. The solution parameters demonstrated that the dissolution of carbendazim in each alcohol was an endothermic process of entropy increase. The change of standard Gibbs free energy illustrated that the dissolution process became more difficult when the carbon chain in the alcohols got longer.

1. Introduction

Carbendazim (Methyl benzimidazol-2-yl carbamate, CAS Registry No.10605-21-7, presented in Fig. 1) is one of the benzimidazole fungicides, which is a widely-used broad-spectrum fungicide [1,2]. Carbendazim can prevent and control fungus for most fruits and crops such as banana, mango, sugar beet and corn [3], whose bactericidal action is realized by selectively disrupting the mitosis of the microtubules and centrosome in the fungus [4]. For the excellent bactericidal effect, carbendazim is widely used in China, India and many other agricultural countries [5,6]. Besides, carbendazim can also be used as an industrial anti-corrosion agent [4].

Carbendazim is normally synthesized through a two-step method [7]. The intermediate methyl cyanocarbenmate is first prepared by the reaction of methyl chloroformate with cyanamide, and then methyl cyanocarbenmate reacts with orthophenylene diamine to form carbendazim at a temperature over 373.15 K with the solvent of alcohols [8,9]. After a cooling crystallization, carbendazim was obtained with a yield of 65–80% [9]. To optimize the crystallization process for a higher yield [10,11], the solution thermodynamic data of carbendazim was needed. Up to date, the research work was mainly focused on the toxicity [12,13] and detection [14,15] of carbendazim, however, no solubility data was found in literature.

In this work, the solubility of carbendazim in five lower alcohols (Methanol, Ethanol, *n*-Propanol, *n*-Butanol, and *n*-Pentanol) at temperatures ranging from 278.15 K to 323.15 K was measured using the laser detecting technique. The solubility data was correlated using Apelblat equation, and the dissolving enthalpy and entropy were estimated according to the Van't Hoff equation. Moreover, the Gibbs free energy was calculated for the dissolution process of carbendazim.

2. Experimental section

2.1. Materials

Carbendazim (mass fraction > 99.0%) was supplied by Jiangsu Lanfeng Co., Ltd. China. The sample was tested by X-ray powder diffraction (XRD), differential scanning calorimetry (DSC) and thermogravimetric (TG), and the results were presented in Fig. 2(a) and Fig. 3. In the TG curve of Fig. 3, the mass loss was obvious at the temperature range of 240–260 °C as carbendazim degraded. Simultaneously, an endothermic peak was observed in the DSC curve, and the peak temperature (T_p) is 255 °C. The alcohols (Methanol, Ethanol, *n*-Propanol, *n*-Butanol, and *n*-Pentanol) were purchased from Kemiou Chemical Reagent Co., Ltd. China. All the chemicals were of highest purity commercially available and directly used without further purification. The detailed information about materials used in this work is shown in Table 1.

2.2. Solubility measurements

The solubility of carbendazim in the lower alcohols was measured from 278.15 K to 323.15 K by a dynamic thermodynamic equilibrium method with the laser detecting technique, and the apparatus was the same as that in the literature [16,17]. A certain amount of solvent was transferred into the jacketed glass crystallizer which was equipped with a condenser for preventing the volatilization. The temperature, controlled by the water bath device (SHP DC-2015, China), was accurately

* Corresponding author.
E-mail address: lcsong@hit.edu.cn (L. Song).

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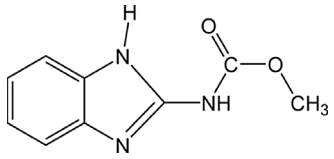

Fig. 1. Molecular structure of carbendazim.

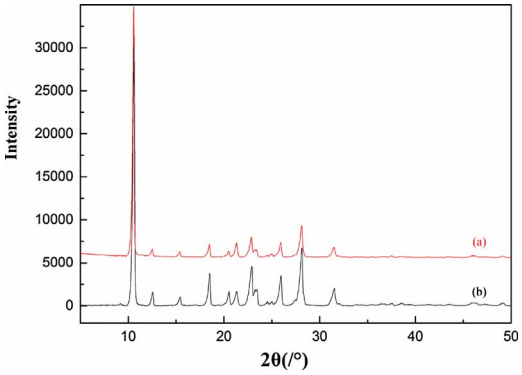

Fig. 2. X-ray diffraction patterns of carbendazim: (a), the material used in this study; (b), the solid phase in solubility equilibrium.

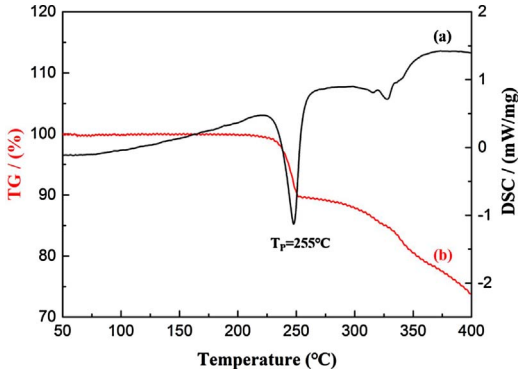

Fig. 3. Thermal analysis of carbendazim: (a), DSC curve; (b), TG curve.

Table 1
Description of Materials Used in This Paper.

Chemical name	Source	Final mass fraction purity	Analysis method[a]
Carbendazim	*A*	> 99.0%	HPLC
Methanol	*B*	99.8%	GC
Ethanol	*B*	99.8%	GC
n-Propanol	*B*	99.8%	GC
n-Butanol	*B*	99.8%	GC
n-Pentanol	*B*	99.8%	GC

A, Jiangsu Lanfeng Group Chemistry Co., Ltd China.
B, Tianjin Kemiou Chemical Reagent Co., Ltd China.
[a] The purity analysis was completed by the suppliers.

measured with a mercury thermometer (uncertainty 0.05 K). The solvent inside was stirred by a magnetic stirrer, while the weighed solute was added. The solution became clear when the solute was completely dissolved. Simultaneously, the intensity of the laser penetrating the solution reached its maximum. Then another amount of weighed solute was added. This procedure was repeated until the last addition couldn't be dissolved completely. Thus the solubility range of this data point could be determined by the total mass of the solute added before and after the last addition. A new measurement experiment was designed according to the solubility range obtained from the previous experiment, in which a one-time delivery of the solute dissolved in the previous experiment was performed, and the measurement experiment was then carried out with less amount of solute each addition. In this way, the solubility range was continuously narrowed by another new experiment and also the fewer times of solute addition was consumed to reduce the accumulated error. The solubility value was finally determined when an addition (2–5 mg, less than 1% of the dissolved carbendazim) couldn't be dissolved completely in 1 h. During the experiment, the solvent and solute were weighed by an electronic balance with uncertainty of ± 0.0002 g (Toledo AB204-S, Switzerland). The data was recorded and used for the calculation of the mole fraction solubility (x_0) of carbendazim according to Eq. (1). All the experiments were repeated at least three times to confirm the data point.

$$x_0 = \frac{m_0/M_0}{m_0/M_0 + m_1/M_1} \tag{1}$$

where letter m_i and M_i (g/mol) represent the mass and the molar mass values of solute ($i = 0$) and solvent ($i = 1$), respectively. The crystal structure of solid phase in solubility equilibrium was determined using an X-ray diffractometer (Rigaku D/max-2500).

3. Results and discussion

3.1. Solubility data of carbendazim

The XRD pattern of the solid phase in solubility equilibrium was shown as Fig. 2(b), which demonstrated that the structure of carbendazim remained unchanged in the solubility measurement, no new polymorph or solvate were found. The solubility of carbendazim in the five alcohols (Methanol, Ethanol, *n*-Propanol, *n*-Butanol, and *n*-Pentanol) at the temperatures from 278.15 K to 323.15 K is listed in Table 2 and plotted in Fig. 4. Fig. 4 shows that the solubility of carbendazim increases with the increasing temperature in each solvent. The solubility of carbendazim in different solvents ranks as: Methanol > Ethanol > *n*-Propanol > *n*-Butanol > *n*-Pentanol. The result can be due to the ion-dipole type interaction between the solute and solvent, which enhances the solubility [18]. All the solvents are alcohols which have the similar structure and the same hydroxyl functional group, and the polarity values are listed as: Methanol (76.2), Ethanol (65.4), *n*-Propanol (61.7), *n*-Butanol (60.2), *n*-Pentanol (56.8) [19]. The carbon chain in the alcohol decreases its polarity, which weakens the ion-dipole type interaction between the solute and solvent, and lowers the solubility of carbendazim correspondingly.

3.2. Correlation of carbendazim solubility

Apelblat equation [20], shown as Eq. (2), is an effective model used to fit the solubility with temperature in pure solvent, which is derived from the relationship of ideal solid–liquid equilibrium equation [21].

$$\ln x_0 = a + \frac{b}{T} + c\ln T \tag{2}$$

where a, b, and c are the model parameters and T is absolute temperature (K). The experimental solubility data of carbendazim was correlated by Apelblat equation, and the parameters regressed using least square method were listed in Table 3, with which the calculated solubility values were obtained and listed in Table 2. Correspondingly, the relative deviation (RD) and root-mean-square deviation (RMSD) were calculated according to Eqs. (3) and (4) respectively.

$$\mathrm{RD} = \frac{x_0 - x_0^{cal}}{x_0} \tag{3}$$

$$\mathrm{RMSD} = \left\{\frac{1}{N_i}\sum_{i=1}^{N}\left(x_0^{cal} - x_0\right)^2\right\}^{1/2} \tag{4}$$

where x_0 and x_0^{cal} are the experimental and calculated values of the mole fraction solubility and respectively, and N is the number of